山形大学紀要（工学）第14巻　第2号　昭和52年2月
Bull. of Yamagata Univ. Eng., Vol. 14 No. 2 Feb. 1977

Palladium-catalyzed Homogeneous Reduction of α,β-Unsaturated Esters and Aromatic Nitro Compounds.

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(Received September 20, 1976)

Abstracts

Aromatic nitro-compounds are not normally reduced by sodium borohydride in aqueous solution or alcoholic solution. The present paper described the use of dichlorobis(triphenylphosphine)palladium (II) as catalysts for this reaction. In a nitrogen atomosphere, nitrobenzene was smoothly reduced at 60°C by sodium borohydride, using triphenylphosphine palladium complex as catalysts to aniline (63%) accompanied by a small amount of hydrazobenzene (3%). In the same conditions, both azoxybenzene and azobenzene were reduced to hydrazobenzene, benzylideneaniline gave benzylaniline (85%), and ethyl cinnamate was led to ethyl hydrocinnamate (75%).

Introduction

Partial reduction of multifunctional unsaturated compounds, using a variety of reagents or catalysts, is of considerable synthetic utility. In all preparatively useful conversions, it is of utmost importance that the reduction is selective as to site. Althogh ketones and aldehydes may be selectively reduced by sodium borohydride, only few examples are to be found in the literature of the reduction of nitro compounds by complex borohydrides, and it is generally reported that nitro group are reduced either with difficulty or not at all by borohydride.[1,2] Recently, however, it has been observed that reduction of aromatic nitro group was smoothly reduced with sodium borohydride in the presence of suitable catalysts such as palladium chloride,[3] bipyridyl cobalt complex.[4] cyano cobalt complex,[5] cyano nickel complex,[6] triphenylphosphine nickel complex,[7] and dimethylformamide rhodium complex.[8] In relation to the reduction of nitro group with borohydride, we wish to report that, in the presence of dichlorobis (triphenylphosphine)-palladium (II). aromatic nitro compounds were smoothly reduced with sodium

borohydride to corresponding amine compounds accompanied by a small amount of hydrazo-derivatives, and α,β-unsaturted esters such as ethly cinnamate were also reduced to the corresponding saturated esters.

Experiment

Measurement. The melting and boiling points are uncorrected. The IR spectrum was measured using a Hitachi 215 spectrophotometer. Gas-chromatographic analyses were carried out on a column, silicon SE 30 (5% on celite), 1 m at 110°C, with a Hitachi K-53 gas-chromatograph.

Chemicals. Dichlorobis(triphenylphosphine)palladium(II) was prepared by the method described in the literature.[6] Sodium borohydride, nitro compounds, and α,β-unsaturated esters of a commercial grade were used without further purification.

Reduction Procedure. In a nitrogen atomosphere, to the solution of dichlorobis(triphenylphosphine)palladium(II) (1.40g, 2 mmol) in 80 ml of absolute ethanol, 10 mmol of the material to be reduced and then 1.13g (30mmol) of sodium borohydride were added gradually and the reaction mixture was stirred for 6 hr at 60°C. After cooling, 100 ml of water was added and the solvent was removed under reduced pressure.

In the case of tne reduction of aromatic nitro compounds, azoxybenzene, and azobenzene, after extraction with ether and followed evaporation of the ether, the products were purified by column-chromatography (Al_2O_3-CCl_4) and were identified by a obeservation of IR spectra and by a mixed-melting-point determination with an authentic sample.

In the case of the reduction of benzylideneaniline and α,β-unsaturated esters, all reaction mixture were analyzed by gas-chromatography. Only one product was detected in all cases. The products were isolated and all IR spectra obtained were compared with those of authentic samples.

These results were given in Table 1.

Table I. Reduction of Aromatic Nitro Compounds and α,β-Unsaturated Esters with $NaBH_4$-$(Ph_3P)_2PdCl_2$.

Substrate	Products (yield, mp or bp°C).
nitrobenzene	aniline (63%, bp 183) hydrazobenzene (3%, mp 126[a])
p-nitrotoluene	*p*-toluidine (65%, mp 44-45[b]) 1,2-di(4-tolyl)hydrazine (4%, mp 135[c])

o-nitrotoluene	*o*-toluidine (60%, bp 200-202[b]) 1,2-di(2-tolyl)hydrazine (4 %, mp 162[d])
p-nitroanisole	*p*-anisidine (67%, mp 57[d]) 1,2-di(4-anisyl)hydrazine (3 %, mp 131-132[e])
p-chloronitrobenzene	*p*-chloroaniline (58%, mp 70[f]) 1,2-di(4-chlorophenyl)hydrazine (4 %, mp 124[g])
p-bromonitrobenzene	*p*-bromoaniline (62%, mp 66[d]) 1,2-di(4-bromophenyl)hydrazine (4 %, mp 130[h])
ethl y*p*-nitrobenzoate	ethyl *p*-aminobenzoate (60%, mp 89[i]) 1,2-di (4-ethoxycarbonylphenyl) hydrazine (3 %, mp 118[j])
azobenzene	hydrazobenzene (82%, mp 126[a])
azoxybenzene	hydrazobenzene (80%, mp 126[a])
dinzylideneaniline	benzylaniline (85%, mp 37-38[k])
ethyl cinnamate	ethyl hydrocinnamate (75%, bp 245[l])
ethyl crotonate	ethyl butyrate (62%, bp 119-120[m])
methyl methacrylate	methyl isobutyrate (60%, bp 90-92[n])
ethyl maleate	ethyl succinccinate (64%, bp 217[o])
ethyl fumarate	ethyl succinate (60%, dp 217[o])

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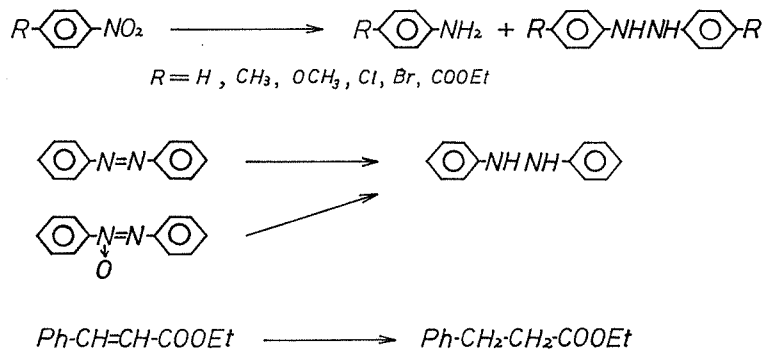
Discussion

Sodium borohydride- $(Ph_3P)_2PdCl_2$ is a very versatile reducing agent, as evidenced by the data in Table 1. Previously it has been reported that in the



presence of cyano nickel complex the reduction of nitrobenzene with sodium borohydride led to the formation of azoxybenzene as a main product.[6] Arai and coworkers[10] also described that nitrobenzene was converted to a nearly equimolar mixture of aniline and azoxybenzene by sodium borohydride catalyzed by cobalt ammine complexes. In our investigation, however, aromatic nitro compounds were smoothly reduced to the corresponding amine derivatives accompanied with a small amount of hydrazobenzene derivatives. Moreover, in the same conditions both azobenzene and azoxybenzene were converted to hydrazobenzene and no aniline was detected. These data indicate that, in the reduction of nitro compounds, the formation of amine derivatives proceeds *via* the hydrogenolysis of the nitrogen-oxygen σ bond rather than *via* the hydrogenolysis of the nitrogen-nitrogen σ bond (the hydrogenolysis of hydrazobenzene). The formation of hydrazobenzene seems to proceed *via* the condensation of nitrosobenzene and phenylhydroxylamine,[11] which both of them were the reduction intermediates of nitrobenzene. On the other hand, in the same conditions benzylideneaniline was reduced to benzylaniline in a good yield. It suggests that the carbon-nitrogen π bond is easily reduced but the carbon-nitrogen σ bond does not undergo hydrogenolysis. In addition, the data in the Table 1 indicate that the carbon-halogen bond and ester group were unaffected in such a reaction with borohydride-$(Ph_3P)_2PdCl_2$.

Similarly to the reduction of nitro group only with sodium borohydride, the employment of sodium borohydride to reduce carbon-carbon double bond has not been wide-spread,[1] and there are but few references to such use.[12-15] It was reported[14] that ethyl atropate was reduced to ethyl hydratropate only with sodium borohydride in ethanol, whereas, its structural isomer, ethyl cinnamate was unaffected under the same conditions, and he suggeeted that the failure of ethyl cinnamate to undergo the reduction with borohydride is probably due to the lack of a relatively strong and localized electrophilic center brought about by conjugation of the double bond with the β-phenyl group. However, in the

presence of $(Ph_3P)_2PdCl_2$, ethyl cinnamate was smoothly reduced by sodium borohydride to ethyl hydrocinnamate, and α,β-unsatureted esters such as ethyl crotonate, methyl methacrylate, ethyl maleate, and ethyl fumarate were also reduced to the corresponding dihydro-derivatives (Table 1). Green and Munakata[16] reported that, although the isolation of stable hydrido-palladium complex by the reduction of tertiary phosphine palladium complex with sodium borohydride was unsuccessful, the stable complex *trans* $(Cy_3P)_2PdHCl$ (where Cy is cyclohexyl) was obtained from tertiary phosphine palladium complex using *'trans*-$(Cy_3P)_2NiH(BH_4)$ as a reducing agent. Thus, it seems to be assumed that the reduction of α,β-unsaturated esters with borohydride-$(Ph_3P)_2PdCl_2$ proceeds *via* the formation of palladium hydride complex and the following mechanism is assumed.

$$(Ph_3P)_2PdCl_2 + NaBH_4 \longrightarrow (Ph_3P)_2PdHCl \quad (1)$$

$$RCH=CHCOOR' + (Ph_3P)_2PdHCl \longrightarrow RCH=CHCOOR' \longrightarrow HPdCl(Ph_3P)_2$$

$$RCH_2CH(COOR')PdCl(Ph_3P)_2 \quad (2)$$

$$RCH_2CH(COOR')PdCl(Ph_3P)_2 + NaBH_4 \longrightarrow RCH_2CH_2COOR' + HPdCl(Ph_3P)_2 \quad (3)$$

Insertion of the coordinated double bond into the hydrido-palladium intermediate would give a σ bonded alkyl-palladium intermediate (reaction 2), which is easily converted to saturated compound by sodium borohydride. Reduction of σ bonded alkyl-palladium compounds with sodium borohydride have been reported[17] to proceed smoothly even at room temperature.

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α,β-不飽和エステルおよび芳香族ニトロ化合物のパラジウム触媒による均一還元

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芳香族ニトロ化合物とα,β不飽和酸のエステルは一般には水素化ホウ素ナトリウムにより，そのニトロ基および炭素—炭素二重結合は還元されない。触媒量のパラジウム錯体の存在で芳香族のニトロ基，α,β不飽和エステルの二重結合が水素化ホウ素ナトリウムによって還元されると云う結果がえられたことを報告する。ニトロベンゼンは窒素雰囲気下ジクロロービス（トリフエニルホスヒン）パラジウム（Ⅱ）の存在で水素下ホウ素ナトリウムにより還元されアニリン（63%）とヒドラゾベンゼン（3%）を生ずる。アゾベンゼンおよびアゾオキシベンゼンは同一条件下でそれぞれヒドラゾベンゼンを生ずる。ベンジリデンアニリンはベンジルアニリンに桂皮酸エチルエステルは同様にヒドロ桂皮酸エチルエステルに還元された。